# (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

## (19) World Intellectual Property Organization

International Bureau





(43) International Publication Date 14 October 2004 (14.10.2004)

### (10) International Publication Number WO 2004/087996 A1

(51) International Patent Classification7:

C23F 11/16

(21) International Application Number:

PCT/GB2004/001373

(22) International Filing Date: 30 March 2004 (30.03.2004)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 0307290.7

31 March 2003 (31.03.2003)

(71) Applicant (for all designated States except US): MID-DLESEX SILVER CO. LIMITED [GB/GB]; Middlesex University, Queensway, Enfield, Middlesex EN3 4SA (GB).

(72) Inventors; and

- (75) Inventors/Applicants (for US only): JOHNS, Peter, Gammon [GB/GB]; 39 Richmond Drive, Watford, Hertfordshire WD17 3BQ (GB). HARRISON, Clare, Elizabeth [GB/GB]; 23 Salmons Road, Edmonton N9 7JT (GB).
- (74) Agent: COLE, Paul, Gilbert; Lucas + Co., 135 Westhall Road, Warlingham, Surrey CR6 9HJ (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

### Declaration under Rule 4.17:

of inventorship (Rule 4.17(iv)) for US only

#### **Published:**

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ENHANCING SILVER TARNISH-RESISTANCE

(57) Abstract: An alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide may be used to surface treat of an alloy of silver containing an amount of germanium that is effective to reduce firestain and/or tarnishing. The treatment has been found to further reduce tarnishing of the alloy such that a sample can be supported close above a 20% solution of ammonium polysulphide for at least 30 minutes while retaining a generally untarnished appearance. The treatment may be carried out at the end of manufacturing a shaped article to give rise to an article that will preserve its untarnished appearance both during transit to a point of sale but during subsequent display for an extended period. The invention therefore also includes a method for manufacturing a tarnish-resistant silver article, which comprises the steps of forming a shaped article of an alloy of silver containing an amount of germanium that is effective to reduce firestain and/or tarnishing, surface treating the article with an alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide; and introducing the article into packaging. Also disclosed for use in treating an alloy of silver as aforesaid is a water-based composition comprising a treatment agent selected from an alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide and a mixture of an anionic surfactant and an amphoteric or nonionic surfactant in a concentration that is effective to solubilise the treatment agent.